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Title of Invention: Method of manufacturing porous  
ceramic supports

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## Specifications

1. Title of Invention:

Method of manufacturing porous ceramic supports

2. Claims:

A method of manufacturing porous ceramic supports, in which a gas atmosphere consisting of organic metal compounds or inorganic compounds is made surrounding a porous ceramic body, this gas atmosphere is heated to decompose it, and fibers or whiskers of inorganic compounds produced by the decomposition of this gas are formed on the surface of the porous ceramic body.

3. Detailed Explanation of Invention:

Industrial Field of Application

This invention concerns a method of manufacturing porous ceramic supports.

Up to now, the method disclosed in the Specifications of U.S. Patent No. 4,264,346 has been used as such a method.

That is, ceramic fibers, such as  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , etc., are accumulated on the surface of a porous ceramic body with a three-dimensional reticular skeleton, and these fibers are fixed with an organic binder.

This method, however, has the problem that it is difficult to accumulate the fibers uniformly on the surface of the skeleton of the porous ceramic body.

This invention was made with this problem in mind; its

purpose is to produce needle-shaped inorganic compounds, such as fibers, uniformly on the surface of a porous ceramic body.

The purpose of this invention is achieved by forming a gas atmosphere consisting of organic metal compounds or inorganic compounds surrounding a porous ceramic body with a three-dimensional reticular structure, heating this gas atmosphere to decompose it, and forming fibers or whiskers of inorganic compounds produced by the decomposition of this gas on the surface of the porous ceramic body.

In this invention, when the aforementioned gas atmosphere is heated, a plasma is produced in this atmosphere at the same time, which helps to decompose the gas.

The term "organic metal compound or inorganic compound" in this invention refers to methylsilane trichloride, 4-aminosilicon (the above are "organic metal compounds"), zirconia chloride compounds, boron chloride, silane (the above are "inorganic compounds"), etc.

In this invention, gases of these compounds can be used as is, or carrier gases such as argon, oxygen, or nitrogen can be bubbled in solutions of these compounds so that the compounds are contained in the carrier gases.

By decomposing the gases mentioned above, in this invention, particle nuclei consisting of inorganic compounds are formed on the surface of the porous ceramic body, and

these grow to become fibers or whiskers. Therefore, fibers or whiskers are formed uniformly on the surface of the porous ceramic body, and the whole surface is covered with depressions and elevations. Furthermore, whiskers and fibers may be present in a mixed state or one or the other alone may be present.

Fig. 1 shows this state schematically. In Fig. 1, 1 is the three-dimensional reticular skeleton of the porous ceramic body; spaces 1a are formed in this skeleton 1. 2 is a fiber or whisker. This fiber or whisker has a needle-shaped structure and is formed on the surface of the skeleton 1.

The presence of these fibers or whiskers serves to increase the surface area of the porous ceramic body. Therefore, when this porous ceramic body is used as a support for a particulate collecting filter in a diesel engine, the efficiency of the collection of the particulates can be increased. Furthermore, when it is used as a support for catalysts for cleaning CO, HC, and NO<sub>2</sub> in exhaust gases, the cleaning performance can be improved.

The porous ceramic body in this invention is covered [? - *hard to read*] by the aforementioned gas atmosphere; this gas may be made to flow, or it may be static.

In this invention, the porous ceramic body need not be limited to ones with three-dimensional reticular structures, as stated above; it may also have a honeycomb structure,

with numerous pathways running through it.

Furthermore, in this invention, the thermal decomposition temperature of the gas, the time the porous ceramic body is held in the gas atmosphere, the temperature of the gas, etc., can be selected so that they are suitable for each embodiment of the invention.

This invention will be explained in more detail below by giving specific working examples. First, an example of a manufacturing device will be described. In Fig. 2, the porous ceramic body 1 is placed in a quartz glass reactor 3, around which a coil 4 which carries a high-frequency current is formed. This coil 4 is electrically connected to a high-frequency current generating source 5. Furthermore, the device is made so that water flows inside the coil 4 in order to keep down the Joulean heat caused by the high-frequency current.

A heater 8, with a heater wire 7 embedded in an insulating material 6, is placed around the outside of the coil 4. The heater wire 7 is electrically connected to an alternating current source 9.

A gas is introduced into the aforementioned reactor 3. That is, as will be explained in the working examples described below, a solution 11 of an organic metal compound or an inorganic compound is introduced into a vessel 10. These compounds may also be introduced as gases into the vessel 10. Oxygen or nitrogen gas is introduced into this

vessel through pipe 12. This gas bubbles in the solution 11 and the vapor of this solution is introduced into the reactor 3, together with the aforementioned nitrogen or argon [sic] gas, through the pipe 13. Furthermore, the quantity of the gas introduced is regulated by the valve 14.

The gas expelled from the reactor 3 passes through the pipe 16 and is cooled and liquefied by a cooling medium 15, such as water, dry ice, or liquid nitrogen. The organic gas is removed by the trap 17.

The liquefied gas is expelled by the vacuum pump 19, with its flow rate regulated by the valve 18. In this figure, furthermore, 20 is a vessel and 21 is a manometer.

Next, the details of the manufacturing method will be explained by giving working examples.

#### Working Example 1

After a porous ceramic body 1 was inserted into the reactor 3, the valve 14 was closed and the valve 18 was opened. The pressure inside the reactor 3 was made  $10^{-5}$  [to  $10$ ] $^{-4}$  torr by means of the vacuum pump 19. On the other hand, argon gas was introduced by means of the pipe 12 and bubbled through the methylsilane trichloride solution in the vessel 10, causing the argon gas to contain silane gas. The valve 14 was opened and this gas was introduced into the reactor 3; the pressure in the reactor 3 was kept at 0.1-10 torr. Next, current was passed through the heater wire 7 and

the ceramic body 1 was heated at 600-1400°C for 0.2-4 [? - hard to read] hours. At the same time, on the other hand, a high-frequency current was passed through the coil 4, producing a plasma in the reactor 3 by means of this high frequency, and the methylsilicon [sic] trichloride gas in the reactor 3 was decomposed. In this manner, silicon carbide fibers or whiskers were produced on the surface of the porous ceramic body 1. Some of the chlorine, hydrogen chloride, etc., gases produced at this time were carried away through the pipe 16 and removed by the trap 17 or dissolved in water, thus preventing deterioration of the vacuum pump 19.

When the porous ceramic body with silicon carbide whiskers or fibers adhering to it, which was produced in this manner, was used in the exhaust system of a diesel engine (2.2 l), and the particulate collection efficiency of the diesel engine, running under the conditions of 2000 revolutions 6 kg m [? - hard to read], was measured. As a result, the efficiency was approximately 55-60%, and the pressure loss was 30-40 MPa.

When a conventional filter with no silicon carbide whiskers or fibers was used, the collection efficiency was 40-45% and the pressure loss was 60-70 MPa. Therefore, the performance of the filter was markedly improved by Working Example 1 of this invention. Furthermore, the fibers or whiskers adhered very strongly to the porous ceramic body;

they were not separated even when a one-hour durability test was performed at a vibration strength of 30 G. Furthermore, the filter underwent almost no change even when used for approximately 100,000 km in a vehicle.

As the porous ceramic body in this working example, a body was used which was made by adhering a slurry the principal ingredient of which was cordierite to an organic three-dimensional reticular structure, e.g., a polyurethane foam, drying it, and firing it for 2 to 15 hours at 1300-1450°C. Besides cordierite, the material used may be ordinary mullite, alumina, silica, zirconia, etc.; there are no limitations on it.

When the porous ceramic body with whiskers or fibers adhering to it which was made by this manufacturing method was used to support platinum on its surface at 0.01 wt %, and this was used as a support for a catalyst for cleaning organic substances in the exhaust from a gasoline engine, it was possible to clean 98-99% of the carbon monoxide and 95-99% of the hydrocarbons under the conditions of 2 liters of engine exhaust and an engine rotation rate of 2000 rpm 6 kg m [sic].

## Working Example 2

In Working Example 1, silicon carbide fibers or whiskers were used, but in this working example, whiskers or fibers of silicon nitride were formed on the porous ceramic body.



The manufacturing method used the same device as in Fig. 2; a 4-aminosilicon solution was put into the vessel 10 and argon gas was introduced and bubbled in it. The argon gas containing 4-aminosilicon gas was introduced into the reactor 3 and the pressure in this reactor 3 was adjusted to 0.1-10 torr. A plasma was produced in the reactor 3 for 0.2-4 hours, in the same manner as in Working Example 1, and the heating temperature of the heater wire 7 was the same as in Working Example 1.

By using this method, silicon nitride whiskers or fibers were adhered to the surface of the porous ceramic body.

The collection efficiency and pressure loss of the porous ceramic body made in this manner were measured by the same method as in Working Example [1], and the results were the same as in Working Example 1.

Moreover, another method of producing the silicon nitride is to introduce a mixture of silane gas and ammonia gas into the reactor 3 and form silicon nitride whiskers or fibers on the porous ceramic body under a vacuum of 0.1-10 torr. Almost the same relationship between the collection efficiency and the pressure loss as in Working Example 1 was also obtained with the product of this method.

### Working Example 3

Using the same device as in Working Example 1, a solution of a zirconia chloride compound was introduced into

the vessel 10 and oxygen gas was introduced through the pipe 12 and bubbled in the solution, producing oxygen gas containing a gas of the aforementioned zirconia chloride compound. This gas was introduced into the reactor 3 and a vacuum of 0.1-10 torr was formed in it; a plasma was produced at 600-1500°C for 0.2-4 hours, and whiskers or fibers of zirconia oxides (consisting primarily of zirconium oxide) were produced on the porous ceramic body.

The performance of the porous ceramic body made in this manner was almost the same as that shown in Working Example 1.

#### Working Example 4

In this working example, diborane (or boron chloride) and ammonia (nitrogen) were reacted and fibers or whiskers of boron nitride were produced.

The same manufacturing device was used as in Working Example 1; gaseous diborane (or boron chloride) and gaseous ammonia (nitrogen) were fed into the reactor 3, and boron nitride fibers or whiskers were produced on the surface of the porous ceramic body by performing the reaction for 0.2-4 hours under a vacuum of 0.1-10 torr and at a temperature of 600-1300°C.

The porous ceramic body produced in this manner showed almost the same performance as that shown in Working Example 1.

4. Simple Explanation of Drawings:

Fig. 1 is a schematic drawing of a porous ceramic support obtained by the method of this invention and Fig. 2 is a schematic drawing of an example of the device used to embody this invention.

1 ... Skeleton of porous ceramic body. 2 ... Fiber or whisker.

Agent: Noboru Okabe, Patent Attorney

Fig. 1

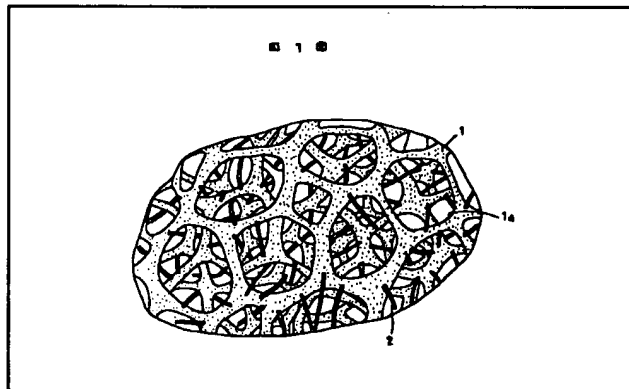
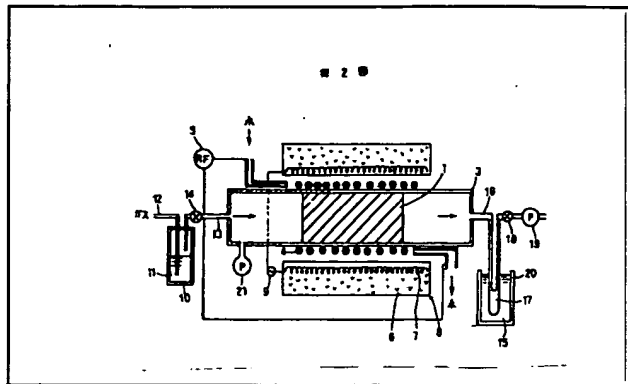


Fig. 2



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